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The catalytic properties and mechanism of cyclohexane/DBSA/water microemulsion system for esterification

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Abstract

A model esterification reaction of hexanol and hexanoic acid in the cyclohexane/dodecylbenzenesulfonic acid (DBSA)/water microemulsion system has been investigated. Compared with cyclohexane/AOT/water microemulsion system and organic medium system, esterification reaction in the cyclohexane/DBSA/water system can perform relatively rapidly whether catalyzed by *Candida cylindracea* lipase (Ccl) or not, this demonstrated that DBSA itself can act as a kind of acid catalyst. Comparison of conversion in several acid-catalyzed reaction systems were also performed and the results showed that the conversion in DBSA system was the most highest, which proved the key factor affecting the conversion was not the acid strength, but the attribute of DBSA as a kind of surfactant. Furthermore, we also perform transesterification reaction of butanol and ethyl butyrate (and methyl butyrate) in the DBSA reverse microemulsion system; however, it cannot get remarkably high conversion like esterification, this reason may be alcohol produced during the transesterification cannot easily enter water droplet like water produced by the esterification. Comparison of conversion in the DBSA system with conversion in the O/W emulsion system DBSA as an emulsion agent also indicated that the conversion in the DBSA reverse microemulsion was much higher. Finally, the mechanism of reaction was also explored. After realizing that DBSA is both acid catalyst and surfactant, we concluded that it was concurrent function of acid catalyst and surfactant that played an important role in improving reaction rate and conversion of esterification.

Keywords: Esterification; Microemulsion; DBSA; Lipase

1. Introduction

It is well known that the direct esterification of carboxylic acid and alcohol, and transesterification of ester and alcohol play important roles in the production of organic esters [1,2]. But to enhance the reaction rate and conversion, we must either make one of the reactants excess or remove the formed alcohol (or water) from products so as to promote the equilibrium process to shift towards the products side. At present, most of the works reported in the literatures have been based on esterification reactions using long-chain length fatty acids and alcohols or short-chain fatty acids and alcohols [3–7]. Catalysts that can be used to catalyze the esterification and transesterification have two main kinds of catalyst, one is chemical catalyst and the other is biocatalyst.

Enzymes are a kind of biocatalyst and are efficient catalyst in synthetic chemistry, their catalytic activity with unnatural substrates attracting much attention because of their much milder reaction conditions and friendly environments [8–14]. In recent years, one of the most intensively studied areas has been the technique of entrapping enzymes in reverse micelles or microemulsion [15,16].

A microemulsion is a thermodynamically stable, isotropic, optically transparent solution consisting of water, oil and a surfactant. Often, the formation of microemulsion requires the presence of a co-surfactant. Depending on the microstructure, microemulsion can be divided into three main cases: an oil-in-water (O/W), a bicontinuous structures, an water-in-oil (W/O) that is aqueous droplets (stabilized by surfactant)

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is dispersed in a continuous organic medium (also called as reverse micelles). For enzyme-catalyzed reactions, a W/O type is usually used. The enzyme is solubilized in the water droplets of the microemulsion, while the oil-soluble substrates are dissolved in the continuous, organic phase. The reactions take place at the oil/water interface and the products are distributed to the oil phase or the water phase [17]. This kind of system mainly has two advantages: (1) lipase molecules can be entrapped in water-containing microdrops, avoiding direct contract with unfavorable organic medium and retaining their catalytic activity. (2) Larger polar/apolar interfacial area improves the interaction between the enzyme and substrates [13–15].

In our work, because reactant hexanol and hexanoic acid are polar organic solvent, they can orient at interface to act as co-surfactant. Although both hexanol and hexanoic acid will decrease with reaction proceeding, there should be a little remanent reactant in the reaction system. So, we think it is more appropriate to call the reaction system as reverse microemulsion system (in short: microemulsion system) in this paper. In the following, we reserve the term microemulsion to our reaction system.

Surfactant is a very important factor in formation of microemulsion system, most of the enzymatic reactions were performed in microemulsion or reverse micelles stabilized by AOT and CTAB surfactant [18–23], few attention has been paid to the other surfactants. So, we initiated our experiment to use DBSA, a relatively cheap and widely used commercial surfactant to form reverse microemulsion. Based on above mentioned, a model esterification reaction of hexanol and hexanoic acid, which was catalyzed by *Candida cylindracea* lipase (Ccl) in DBSA/cyclohexane microemulsion system, was undertaken to compared lipase activity in this system with AOT/cyclohexane microemulsion system and cyclohexane system.

To us surprised, the results of our experiments showed that even if at mild conditions, esterification reaction in the DBSA system can perform very rapidly and obtain relatively considerable conversion whether catalyzed by *C. cylindracea* or not as compared with AOT microemulsion system and organic medium system, this result encouraged us to further explore the reaction mechanism. According to our investigation, we concluded that relatively high conversion in DBSA system is ascribed to the two-fold functions of DBSA, which are surfactant as well as acid catalyst. So, this proved that DBSA microemulsion should be a novel and promising esterification system in improving reaction rate and conversion under relatively mild reaction conditions.

2. Experimental

2.1. Chemicals

Lipase from *C. cylindracea* (specific activity 2.0 unites/mg) was purchased from Fluka; dodecylbenzenesulfonic acid (DBSA, ≈97% purity) was purchased from Tokyo Kasei Kogyo Co. Ltd. (Japan), sodium 1,4-bis (2-ethylhexyl) sulphosuccinate (AOT, ≈96% purity) was purchased from ACROS organics. 2-Naphthalenesulfonic acid (2-NTSA), sodium dodecylbenesulfonic acid (SDBS) and *p*-toluenesulfonic acid (TsOH) were, respectively, obtained from Sigma–Aldrich Co. Ltd. (Germany), chemical factory of Beijing and Xizhong chemical factory of Beijing (China). Hexanoic acid, hexanol, butanol and *n*-ethyl butyrate were all from Shanghai chemical reagent factory (China). Sulfuric acid (H_2SO_4), cyclohexane, *n*-methyl butyrate and *n*-butyl acetate were purchased from Tianjin chemical reagent Co. Ltd. (China). All the other chemicals used were of analytical grade and were used without further purifications.

2.2. Preparation of microemulsion

Microemulsion were prepared by the addition the desired concentration of DBSA (or AOT) to cyclohexane (10 ml). In this mixture, a relevant concentrations buffer (pH 7.0) were then added to, and the final w_0 value was adjusted by the addition of the amount of the buffer. The mixture was briefly shaken until an optically clear single-phase solution was formed.

2.3. Reaction in microemulsion

Both synthesis of esters and transesterification were carried out using above microemulsion by addition of 0.5 mmol hexanol (ethyl butyrate or methyl butyrate) and 1 mmol hexanoic acid (or butanol), the appropriate amounts of lipase was added to initiate reaction. The reaction systems were stirred continuously and incubated at 40 °C for certain times. After some time, samples (200 μl) were withdrawn from the reaction medium, dissolved with ethanol to stop any enzymatic reaction, and then analyzed subsequently by GC.

2.4. Reaction in cyclohexane

The procedure is the same to reaction in microemulsion except that there is not any surfactant (DBSA or AOT) added.

2.5. Reaction in O/W emulsion

In a typical experiment of esterification in O/W emulsion. O/W emulsion was prepared by the addition of amount of DBSA to water (10 ml), then 0.5 mmol hexanol (ethyl butyrate or methyl butyrate) and 1 mmol hexanoic acid (or butanol) were added to the above mixture. The mixture was briefly shaken until white turbid was formed. The procedure performed afterward was the same to the microemulsion.

2.6. Chromatographic analysis

Samples were monitored on a Varian CP-3380 Gas Chromatograph equipped with a FID detector using an Agilent